

I-Optimal Design of Numerous Metals Adsorption by Agro-Waste Activated Carbon

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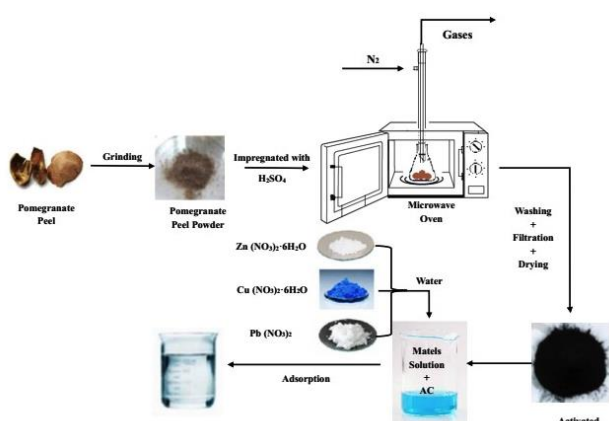
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Graphical abstract



Abstract

This article presents the simultaneous adsorption of numerous metal ions Pb^{2+} , Cu^{2+} , and Zn^{2+} from synthetic solution by activated carbon produced from pomegranate peel (PP) using sulfuric acid and microwave activation. The raw material and pomegranate peel activated carbon (PPAC) were characterized by Brunauer-Emmett-Teller (BET), Field Emission Scanning Electron Microscopy (FESEM), X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) analysis. The effect of absorption time, pH, metal ions concentration, and activated carbon dose on the capacity and adsorption efficiency were investigated. The experimental data of activated carbon preparation and heavy metals adsorption were analyzed by Design-Expert software with I-optimal approach. The statistical analysis for removal efficiencies of Cu^{2+} , Pb^{2+} and Zn^{2+} indicated that the correlation models produced by the software were significant ($P < 0.05$). The maximum removal efficiencies at optimum conditions were obtained in order of $Pb^{2+} > Cu^{2+} > Zn^{2+}$ with 99.373, 98.88 %, and 97.89%, respectively. Adsorption data at equilibrium conditions were fitted with two isotherm models; Langmuir and Freundlich as well as two kinetic models of pseudo first and second order, and the results showed good agreement with Langmuir and second order kinetic model. The results showed that the pomegranate peel activated carbon could be used as an

efficient adsorbent to remove Cu^{2+} , Pb^{2+} and Zn^{2+} from wastewater.

Keywords: Pomegranate peel; Microwave irradiation; Activated Carbon; I-optimal design.

1. Introduction

The availability of potable and clean water is essential to human and animal for healthy lifestyle [Emmanuel 2018]. The environment has a variety of water sources. likes wells, rivers, lakes, ponds, marshes, seas, and oceans possess different qualities and properties. These properties are significantly impacted by human activities and environmental conditions including weather, water location, morphological properties, and vegetations availability in the environment. The weather and climate change affected in water quality (physical, chemical, and biological) due to temperature and rainfall [Bolan *et al.* 2024]. The criteria of water quality for animals' protection from the effects of bio accumulative elements depends on their relative sensitivities and should be lower than that affected to the aquatic living organisms [Wang *et al.* 2022]. Water pollution due to the presence of nonmetals and metals in addition to bacteria or viruses is harmful to the human being health [Witkowska *et al.* 2021; Muhammad *et al.* 2019, 2024]. There are two types of heavy metals which can be classified as essential and non-essential metals depend on its concentration, the essential metals at low-concentration are considered as nontoxic or relatively nontoxic and its useful for the biological activities, various enzymatic reactions, oxygen utilization, bimolecular synthesis, ...etc [Slobodian *et al.* 2024]. The essential heavy metals like Copper (Cu), Cobalt (Co), Iron (Fe), Manganese (Mn), and Zinc [Rengel 1999; Jomova *et al.* 2022; Singh *et al.* 2011]. Whereas the non-essential heavy metals like Arsenic (As), Chromium (Cr), Cadmium (Cd), Lead (Pb), Mercury (Hg), and Selenium (Se) [Tchounwou *et al.* 2012; Saad *et al.* 2016; Balali-Mood *et al.* 2021; Vizuite Zorita *et al.* 2018]. The presence of heavy metals in sources of water have motivated the researchers to find efficient methods of treatment to eliminate these metals from water sources [Álvarez-Ayuso *et al.* 2003; Inglezakis *et al.* 2004; EFFICIENCY ASSESSMENT 2022; Adsorption of Cd(II) 2009; Thermodynamic and Kinetic Study 2013]. Therefore, different methods were applied to remove heavy metals

from water including adsorption, advanced oxidation, electrochemical, Electro-Fenton process, ion exchange, precipitation, and reverse osmosis [Alkhadra *et al.* 2022; Garrido-Cardenas *et al.* 2019; Al-Asheh and Duvnjak 1997; Mohammed *et al.* 2009; Ammar and Jaafar 2017]. Various studies were applied for removing heavy metal from water or wastewater by adsorption method using agricultural wastes such as beech leaves [Salim *et al.* 2008], charred pistachio shell [COMPARATIVE STUDY 2021], coconut husk [Hanafiah *et al.* 2020], oil palm waste [Ayob *et al.* 2021], rice husks [Abbas *et al.* 2020], sawdust [Bulut and Tez 2007; Khalid and Salman 2019], and waste tea leaves [Tee and Khan 1988]. The carbon-based substance as activated carbon has high surface area, various pore structure, and different pores volume, with various functional groups likes aldehydes, carboxyl, carbonyl, phenols [Neolaka *et al.* 2023; Momčilović *et al.* 2011].

However, the commercial activated carbon as efficient adsorber is considered as costly material [Dash 2010; Velempini and Pillay 2019]. Several types of activated carbons were prepared from agricultural by-products, and waste using conventional and microwave methods have garnered increased interest due to their low-cost and availability. The properties of activated carbon mainly depend on the precursors and preparation techniques [Gratuito *et al.* 2008; Jabbar *et al.* 2022; Salman *et al.* 2022; Salman 2020]. Different agricultural wastes and byproducts were used such as bamboo dust [Kannan and Veemaraj 2009], coconut shell kenaf core [Chowdhury *et al.* 2012], coconut shell [Amuda *et al.* 2007], oil palm and empty fruit bunch [Foo and Hameed 2011; Nemr 2009], pecan and almond shells [Toles *et al.* 1997; Ng *et al.* 2003], peach stones and olive stones [Ferro-García *et al.* 1988], rice husks [Khalil *et al.* 2021], rice straw pellets, soybean hull pellets, sugarcane bagasse [Johns *et al.*

1988], sawdust [Khalid and Salman 2019; Shakir 2010], Siri's seed pods [Ahmed and Theydan 2013a, 2013b], water hyacinth [Salman *et al.* 2021] were used to prepared activated carbon adsorbent for various pollutants including mono and bimetals using conventional techniques. Whereas, Microwave as efficient technique was applied for activated carbon peroration using date stones [Optimization of Activated 2014], Ficus benjamina [Sami and Talib 2023; Khatab E. Talib and Salman 2023], plum seed [Salman *et al.* 2024] and different agricultural waste [Hoseinzadeh Hesas *et al.* 2013]. The limitations of these researches including the adsorption of mono and bimetals using activated carbon prepared by microwave techniques or adsorption of multi metal with activated carbon prepared using conventional method have motivated this research. It is essential to investigate the competition impacts, affinity, and selectivity of metals adsorption using a variety of metals [Seo *et al.* 2008; Xiao and Thomas 2004; Srinivasan and Sathiya 2009]. This study focuses the adsorption of multi-metal ions (Pb^{2+} , Cu^{2+} and Zn^{2+}) from solution by activated carbon prepared from pomegranate peel with acid and microwave activation. Sulfuric acid was selected for chemical activation and microwave technique for heating to produce activated carbon preparation. The effect of pH, numerous metal ions concentration, adsorption time, and adsorbent dose on the capacity of adsorption and removal efficiency was investigated. The adsorption process was analyzed using the response surface method (RSM) with I optimal design methodology.

2. Materials and methods

All materials and experimental setup that used in this study are illustrated listed in **Table 1**.

Table 1. Materials and experimental setup

Material	Chemical Formula	Purity	Origin	Application
Pomegranate peel	----	----	Local markets	Raw material
Sulfuric acid	H ₂ SO ₄	99.999%	Germany (Sigma-Aldrich)	Chemical activation
Nitric acid	HNO ₃	98%	Germany (Sigma-Aldrich)	pH adjustment
Sodium hydroxide pellets	NaOH	Pure	Germany (Sigma-Aldrich)	pH adjustment
Distilled water	H ₂ O	100%	Al-Khwarizmi Labs	Preparation and washing
Copper nitrate powder	Cu (NO ₃) ₂ ·6H ₂ O	98%	Germany (Sigma-Aldrich)	Synthetic solution
Lead nitrate powder	Pb (NO ₃) ₂	99%	Germany (Sigma-Aldrich)	Synthetic solution
Zinc nitrate powder	Zn (NO ₃) ₂ ·6H ₂ O	98%	Germany (Sigma-Aldrich)	Synthetic solution
Nitrogen	N ₂	99.9%	Local markets	Microwave activation
Methylene Blue Dye	C ₁₆ H ₁₈ ClN ₃ S	~70 %	Germany (Sigma-Aldrich)	Methylene Blue Number (MBN)
Microwave Oven				
Rated Output 450 - 900 watts				
Microwave Frequency 2450 Hz	---	----	Made in China	Activated carbon preparation

2.1. Methylene Blue Number (MBN)

A stock solution with 50 mg/L of methylene blue dye was produced using 50 mg of the methylene blue dye with 1 liter of distilled water. Then ten samples of diluted

solution ranged from 0.025 to 4 mg/L was prepared from the stock solution with distilled water, and the absorbance of the diluted solution samples were measured using UV-visible spectroscopy ($\lambda = 660$ nm). The

calibration curve of the concentration with absorbance values is illustrated shown in **Figure 1**.

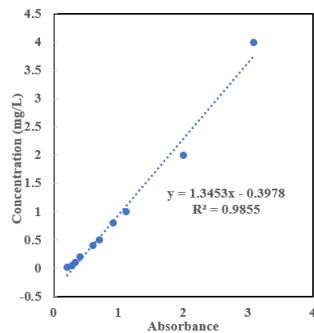


Figure 1. Methylene blue dye calibration curve

2.2. Heavy Metals Solution

Synthetic of aqueous water was prepared for absorption experiments by dissolving metal nitrates in distilled water. A stock solution of Cu (II), Pb (II), and Zn (II) with

100 mg/L for each using annular grade copper nitrate Cu (NO₃)₂·6H₂O, lead nitrate Pb (NO₃)₂, and zinc nitrate Zn (NO₃)₂·6H₂O. The desired concentration for 100 mL of metal ions was prepared from the stock solution varied (10-50) mg/L separately, then mixed together in 300 mL stopper bottles. The pH of solution was adjusted using 0.1 N of HNO₃ and/or NaOH.

2.3. Activated Carbon Preparation

Design Expert Software (13.0) with I-Optimal approach was selected as appropriate method for activated carbon preparation with multi-factor to generate a set number of experiments and reach the response of MBN with a limited number of experimental run trials, and provides a relationship between these multi factors at optimum operating conditions [Waleed Khalid and Salman 2019; Taki and Salman 2024]. The independent factors (multi-factor) levels selected, and number of runs in I-Optimal generated by software are shown in **Tables 2 and 3**.

Table 2. Independent variables of activated carbon preparation

Factors		Levels	
Sulfuric acid concentration (%)	40	60	80
Impregnation ratio IR (ratio)	1:1	1:2	1:3
Impregnation time (hr)	2	4	6
Power of activation (watt)	450	720	900
Time of activation (min)	7	14	21

Table 3. I-Optimal approach for activated carbon preparation

Run	Aced concentration (%)	Impregnation ratio (ratio)	Impregnation time (hr)	Power (watt)	Activation time (min)	MBN (g/g)
1	80	3	4	720	7	24.713247
2	40	3	6	450	7	24.356002
3	40	1	2	900	7	25.13029
4	80	1	6	450	21	25.18612
5	80	1	6	900	7	25.126254
6	40	1	6	900	7	25.05159
7	60	1	4	720	14	25.120873
8	60	1	4	720	14	24.964818
9	40	1	2	450	21	24.804054
10	80	1	2	900	14	24.928629
11	60	3	6	900	14	23.626244
12	80	2	6	450	7	24.938584
13	40	2	4	720	14	24.904952
14	60	3	6	450	21	25.198227
15	40	3	2	900	21	23.677366
16	60	3	2	450	14	24.103826
17	80	1	2	450	7	24.520869
18	60	2	4	900	7	24.376922
19	40	2	4	720	14	25.188138
20	40	1	6	450	14	25.188138
21	40	1	6	900	21	24.522887
22	80	2	4	900	21	23.090949
23	80	2	2	720	21	24.524905
24	40	1	2	450	7	23.678711
25	60	2	4	900	7	24.574008
26	60	2	2	720	7	25.18612
27	60	1	4	720	14	25.079841
28	40	3	4	720	7	24.524232
29	80	3	2	900	14	23.694182
30	40	3	4	450	14	24.470353

2.4. Characterization of Raw Material and Activated Carbon

2.4.1. Brunauer-Emmett-Teller (BET)

The specific surface area, average pore diameter, and pore volume of the pomegranate peels and activated carbon were measured based the maximum value of MBN as indicated in **Table 3** (Run 14) using Brunauer-Emmett-

Table 4. BET test for raw material and AC

Sample	surface area [m^2/g]	Average pore diameter [nm]	Total pore volume($p/p_0=0.990$) [cm^3/g]
Pomegranate peels	8.9671	5.6405	0.012645
activated carbon	1431.8	2.5934	1.623601

Table 5. Composition of pomegranate peels

Element	Atomic %	Atomic % Error	Weight %	Weight % Error
Ca	0.2	0.0	0.5	0.0
K	0.6	0.0	1.5	0.0
C	46.2	0.3	38.6	0.3
Cl	0.2	0.0	0.5	0.0
O	52.8	0.4	58.8	0.4

Table 6. Composition of activated carbon

Element	Atomic %	Atomic % Error	Weight %	Weight % Error
Ca	0.4	0.0	1.2	0.0
K	0.8	0.0	2.1	0.1
C	72.8	0.4	74.5	0.4
Al	0.4	0.0	0.7	0.1
O	25.4	0.5	20.3	0.6
Nb	0.1	0.1	0.7	0.6
Fe	0.1	0.0	0.5	0.1

2.4.2. FESEM & EDX Analysis

The surface morphologies elements composition for peels and the activated carbon produced were analyzed by field emission scanning electron microscopy and energy dispersive X-ray tests. The results of these tests were illustrated in **Figures 2, 3** with **Tables 5 and 6**. **Figure 2** showed that the peels have a uniform surface with large pore diameter and minimal pore sizes, and **Figure 3** depicts a spongy surface with several visible porous with different shapes due to the chemical activation with microwave irradiation. Furthermore, **Tables 5 and 6** stated the elements composition variation of carbon element from 38.6% to 74.5% as compared with other elements composition for peels and the activated carbon due to activation processes [Taki and Salman 2024].

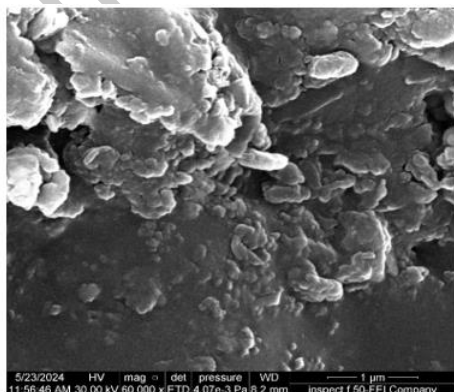


Figure 2. FESEM images of pomegranate peels

Teller technique (USA, HORIBA, SA-900 series). The BET measured data of the pomegranate peels and activated carbon are illustrated in **Table 4**. It's stated from this table that the specific surface area, average pore diameter, and pore volume of the activated carbon were enhanced as compared to pomegranate peels.

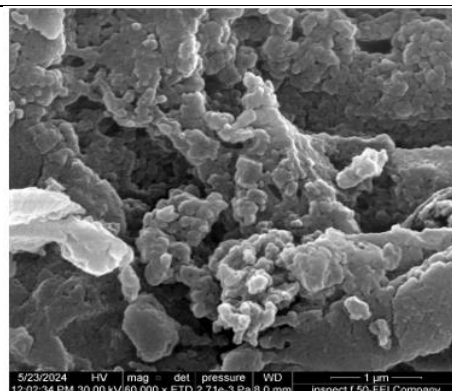


Figure 3. FESEM images of activated carbon

2.4.3. X-ray Diffraction (XRD)

Analysis of peels and activated carbon using X-ray diffraction (XRD) technique as shown in **Figures 4 and 5**. It's from **Figure 4**. **Figure 5** illustrates sharp peaks for activated carbon indicating that the activated carbon primarily possesses amorphous properties with a little crystalline from [Kasaoka *et al.* 1989].

2.4.4. FTIR Analysis

Figure 6 presents the results of the FTIR spectrum analysis for activated carbon (PPAC) and pomegranate peels (PP) between 4000 and 500 cm^{-1} . The strong peaks of the raw material spectrum referred to thier complex nature. Alcohols, phenols, and carboxylic acids exhibit OH stretching, as indicated by the peaks between 3000 and 3500 cm^{-1} [Amaral *et al.* 2020; Nunes Oliveira *et al.* 2016].

The C-H group also designates the peaks between 2500 and 3000 cm^{-1} [Sharma *et al.* 2016]. On the other hand, the peaks between 500 and 1000 cm^{-1} showed the aromatic compounds, while the peaks between 1000 and 1500 cm^{-1} correspond to phenol C=C and aldehyde C=O cm^{-1} [Khare and Baruah 2010; Taşar *et al.* 2014]. Many peak that were distinguished in the raw materials (PP) spectrum were attenuated or vanished in PPAC spectrum. This attenuation compatible with the acid to raw material impregnation which leading to bonds breaking, and new bonds being formation as well as volatile materials emancipation with partially aromatization of non aromatic compounds due to carbonization and activation process [Yagmur *et al.* 2008]. Consequently, OH stretching of alcohols, phenols, and carboxylic acids is indicated by the peaks about 3000–3500 cm^{-1} [Amaral *et al.* 2020; Nunes Oliveira *et al.* 2016]. C-H bending stretching also indicates the peaks between 2500 and 3000 [Sharma *et al.* 2016; Benzaoui *et al.* 2018]. The peaks at 1000–1300 cm^{-1} are assigned to (C–O) bonds because of the presence of hydroxy ester, while the peaks between 1500–1750 cm^{-1} are primarily indicative of alkene C=C and ketones C=O. Similarly, when alkenes are present, the peaks between 600 and 900 cm^{-1} are assigned to =C-H [Jabbar *et al.* 2022].

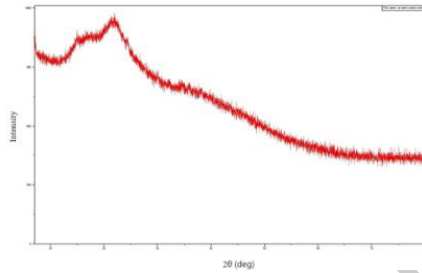


Figure 4. X-ray diffraction of pomegranate peels

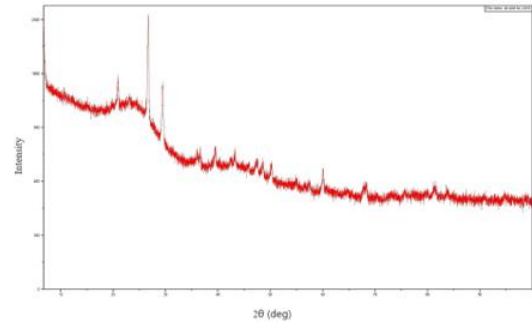


Figure 5. X-ray diffraction of activated carbon

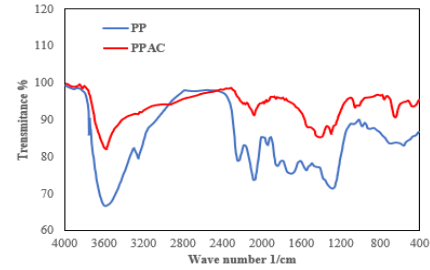


Figure 6. FTIR spectra of pomegranate peels (PP), and activated carbon (PPAC)

3. Results and Discussion

Batch experiments were carried out for adsorption of Pb^{2+} , Cu^{2+} , and Zn^{2+} from synthetic solution simultaneously with different independent factors using I-Optimal approach as efficient for design experiments are illustrated in **Tables 7 and 8**.

Table 7. Independent factors for metals ions adsorption [DESIGN EXPERT]

Factor	Name	Unit	Levels				
A	Contact time	hr	1	2	3	4	5
B	pH	pH	2	4	6	8	10
C	Solution concentration	mg/L	10	20	30	40	50
D	Dose of AC	g/100ml	0.1	0.2	0.3	0.4	0.5

3.1. Adsorption Process Optimization

The removal efficiencies of Cu^{2+} , Pb^{2+} and Zn^{2+} can be described by general quadratic equation (1);

$$Y = \beta_0 + \sum_{i=1}^4 \beta_i X_i + \sum_{i=1}^4 \beta_{ii} X_i^2 + \sum_{1 \leq i < j \leq 4} \beta_{ij} X_i X_j + \varepsilon \quad (1)$$

where Y is model response for Cu^{2+} , pb^{2+} and Zn^{2+} respectively, X_i is independent factor, ε is error of the model, intercept of model, β_0 is intercept of model, β_i , β_{ii} , β_{ij} are linear, quadratic, and interaction coefficients [Saini *et al.* 2019].

Based on the general quadratic equation, the empirical models for predicted removal efficiencies of Pb^{2+} , Cu^{2+} , and Zn^{2+} in coded terms are illustrated in equations 2, 3, 4, **Tables 9**, and the model's fit statistics are given in **Table 10**.

$$RE1\%(\text{pb}) = 99.13 + 2.64A - 2.03B + 2.63C \quad (2)$$

$$-1.12D + 2.47AB + 0.501AC + 5.37AD \\ -0.1348BC - 0.0165BD - 3.35CD - 5.64A^2 \\ -3.38B^2 - 1.54C^2 - 1.18D^2$$

$$RE2\%(\text{Cu}) = 98.69 + 3.41A - 2.28B + 3.55C - 1.18D \quad (3)$$

$$+ 2.77AB + 0.165AC + 6.59AD - 0.2374BC \\ -0.3189BD - 4.31CD - 4.35A^2 - 4.35B^2 \\ -1.34C^2 - 1.74D^2$$

$$RE1\%(\text{Zn}) = 97.46 + 3.93A - 2.46B + 4.7C - 1.53D \quad (4)$$

$$+ 2.44AB + 0.1201AC + 7.36AD - 0.4902BC \\ -0.1082BD - 4.35CD - 7.54A^2 \\ -4.48B^2 - 2.23C^2 - 1.65D^2$$

Table 8. Experimental runs using RSM with I-Optimal method [DESIGN EXPERT]

	Factor 1	Factor 2	Factor 3	Factor 4	Response 1	Response 2	Response 3
Run #	A: Time	B: pH	C: Conc.	D: Dosage	RE1%	RE2%	RE3%
	hr	pH	mg/L	g/100ml	Pb	Cu	Zn
1	3	6	30	0.3	99.2	98.5833	97.3267
2	5	6	20	0.1	86.98	82.475	79.615
3	1	2	20	0.1	94.268	90.335	88.31
4	3	6	30	0.3	99.368	98.5433	97.2267
5	2	6	10	0.2	92.336	90.42	86.79
6	2	10	40	0.5	83.698	79.6225	77.2575
7	1	10	10	0.3	79.248	74.06	69.41
8	1	2	50	0.4	87.5584	84.448	82.156
9	2	4	10	0.5	91.096	88.87	83.73
10	4	2	10	0.3	91.704	89.63	86.34
11	5	2	30	0.5	95.368	94.21	93.61
12	4	2	10	0.3	92.216	90.27	88.11
13	5	10	40	0.2	92.804	91.005	89.13
14	1	8	20	0.5	80.752	75.94	72.99
15	5	10	10	0.5	94.928	93.66	91.17
16	2	10	30	0.2	90.8987	88.6233	87.12
17	3	10	10	0.1	86.68	83.35	80.62
18	1	4	40	0.2	96.314	95.3925	94.2375
19	5	6	50	0.5	97.4272	96.784	96.308
20	3	6	30	0.3	99.373	98.88	97.89
21	1	8	50	0.1	97.0704	96.838	96.406
22	5	6	20	0.1	86.884	83.605	81.845
23	4	2	50	0.1	98.3376	97.922	97.752
24	3	6	30	0.3	98.9973	98.7467	97.58
25	5	4	40	0.3	96.438	95.5475	94.9475

Table 9. Experimental runs with responses predicted values

	Factor 1	Factor 2	Factor 3	Factor 4	Response 1	Response 2	Response 3
Run #	A: Time	B: pH	C: Conc.	D: Dosage			
	hr	pH	mg/L	g/100ml	RE1% (Pb)	RE2% (Cu)	RE3% (Zn)
1	3	6	30	0.3	99.13	98.69	97.46
2	5	6	20	0.1	87.10	83.33	81.24
3	1	2	20	0.1	94.10	90.38	88.30
4	3	6	30	0.3	99.13	98.69	97.46
5	2	6	10	0.2	92.45	90.16	86.77
6	2	10	40	0.5	83.85	79.72	77.83
7	1	10	10	0.3	79.40	74.52	70.29
8	1	2	50	0.4	87.51	84.55	82.28
9	2	4	10	0.5	91.44	89.39	84.76
10	4	2	10	0.3	91.88	89.81	86.83
11	5	2	30	0.5	95.38	94.12	93.69
12	4	2	10	0.3	91.88	89.81	86.83
13	5	10	40	0.2	92.68	90.73	88.78
14	1	8	20	0.5	80.25	75.17	71.28
15	5	10	10	0.5	94.94	93.69	91.21
16	2	10	30	0.2	91.36	89.16	87.70
17	3	10	10	0.1	86.38	82.86	79.73
18	1	4	40	0.2	96.71	95.32	94.28
19	5	6	50	0.5	97.53	96.95	96.28
20	3	6	30	0.3	99.13	98.69	97.46
21	1	8	50	0.1	96.82	96.71	96.18
22	5	6	20	0.1	87.10	83.33	81.24
23	4	2	50	0.1	98.40	97.94	97.78
24	3	6	30	0.3	99.13	98.69	97.46
25	5	4	40	0.3	96.27	95.34	94.73

Table 10. Summary of model's Fit Statistics

RE%	Std. Dev.	Mean	CV%	R ²	Adjusted R ²	Predicted R ²	Adeq Precision
Pb	0.3729	92.4	0.4036	0.9983	0.996	0.9684	68.2884
Cu	0.5462	90.31	0.6048	0.9977	0.9944	0.968	57.1414
Zn	1.08	88.32	1.22	0.9929	0.9829	0.925	32.8762

It's clearly observed from **Table 10**, that the adjusted and predicted R² are in a reasonable agreement (difference < 0.2). Signal to noise ratio for all model are greater than 4, which mean all models are applicable for design range.

3.2. Response Surface Plots

Contour plots for removal efficiencies of Pb²⁺, Cu²⁺, and Zn²⁺ related to the multi-independent factors was applied to explain the interactions between these factors and to validate the optimum values for each factor to obtained maximum removal efficiency of Cu²⁺, Pb²⁺ and Zn²⁺ [Salman *et al.* 20024; Bouazizi *et al.* 2016; Hummadi *et al.* 2021]. The contour plots for multi-metals removal efficiencies versus contact time, pH, metal ions concentrations, and adsorbent doses are shown in **Figures 7, 8, 9, and 10**. **Figures 7a, b, and c**, illustrated the effect of contact time and pH on ions adsorption at constant metal ions concentrations (30 mg/L) and adsorbent dose (0.3g/100mL). It's noted from these figures the ions adsorption increased with increase in in contact time and pH up to 3 hr and pH 6. Furthermore, the adsorption decreases for contact time greater than 3 hr and pH 6. This implied that the active sites in adsorbent were

occupied by heavy metal ions with increasing in desorption rate [Gabaldón *et al.* 2000; Kobya *et al.* 2005]. Likewise, the adsorption rate for pH below 6 mean that the hydrogen ions available in solution was probably to compete with heavy metal ions and for pH greater than 6 the heavy metal ions may be precipitate as hydroxides [Moreno-Piraján *et al.* 2011]. **Figure 8a, b, and c**, illustrated the effect of contact time and metals ions concentration on removal efficiency at constant pH (6) and adsorbent dose (0.3g/100mL). It's noted from these figures the removal efficiency increased with increase in contact time up to 3 hr and 30 mg/L. Whereas, the removal efficiency decreased for contact time, and concentration greater than 3 hr and 30 mg/L. This mean that the active sites in adsorbent were vacuous and ravenous for ions which then occupied by heavy metal ions with increasing of time and concentration consequently, a significant increasing in desorption rate as the contact time increased [Taty-Costodes *et al.* 2003; Kavand *et al.* 2020].

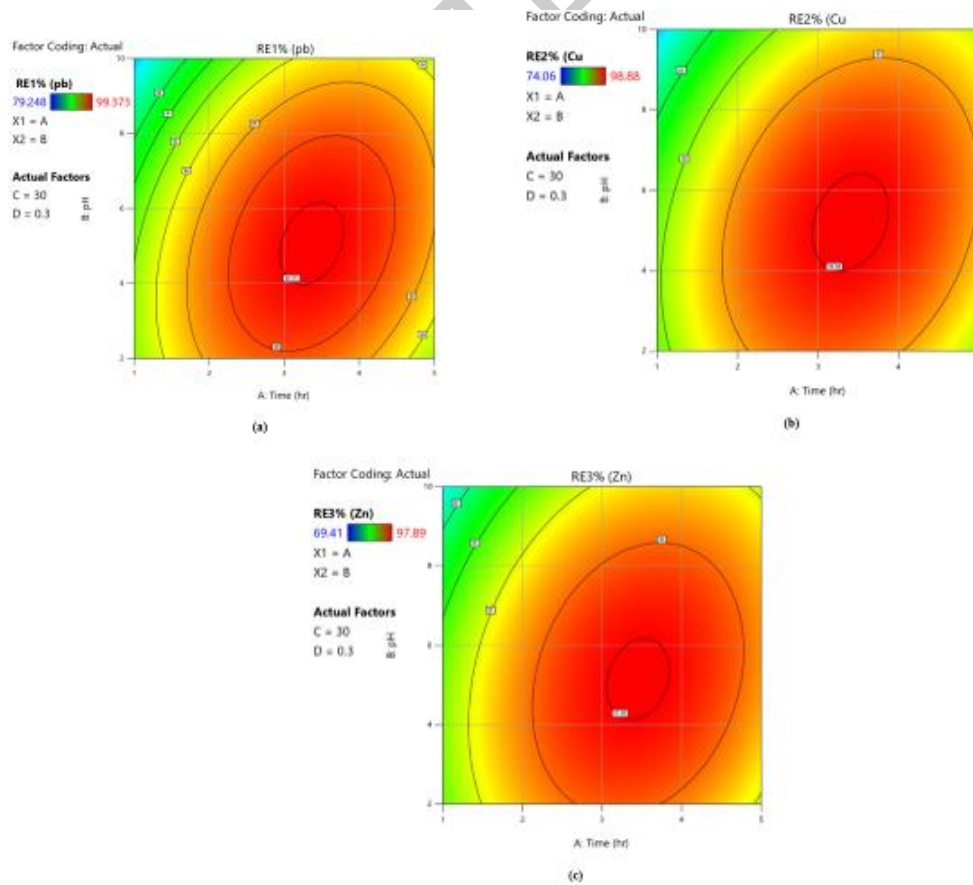


Figure 7 (a, b, c). Contour plots contact time (hr) and pH (metals concentration = 30 mg/L, adsorbent dose = 0.3 g/100 mL)

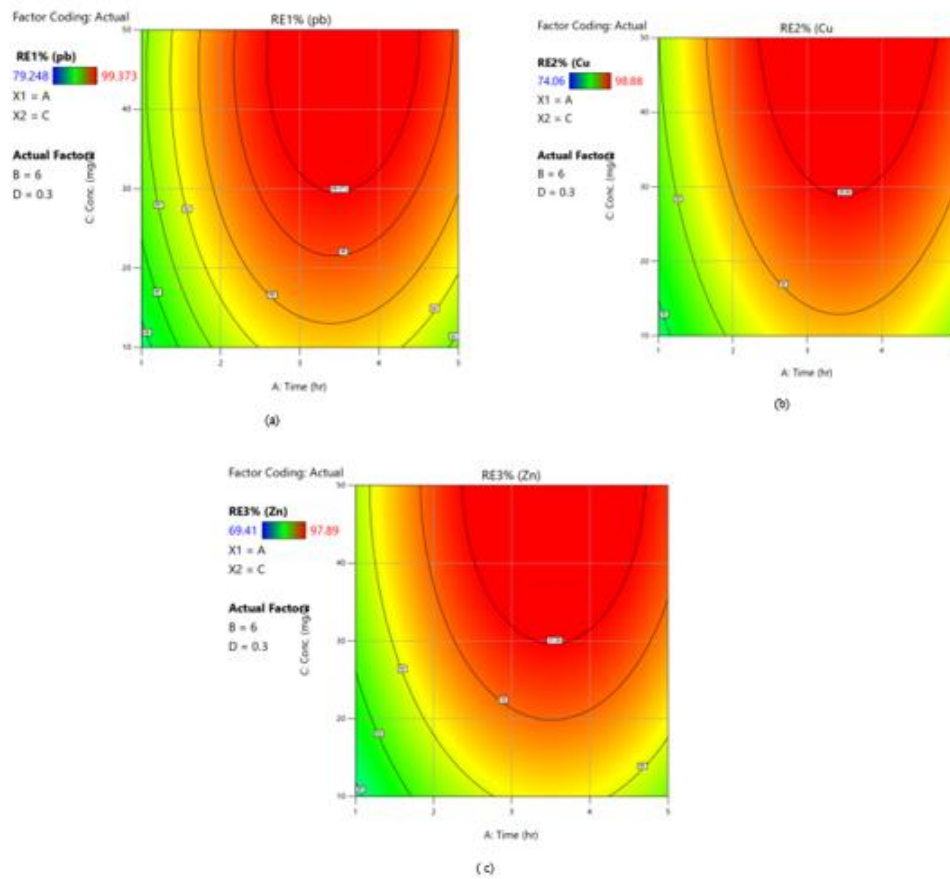


Figure 8 (a, b, c). Contour plots contact time (hr) and metals concentration (pH = 6, adsorbent dose = 0.3 g/100 mL)

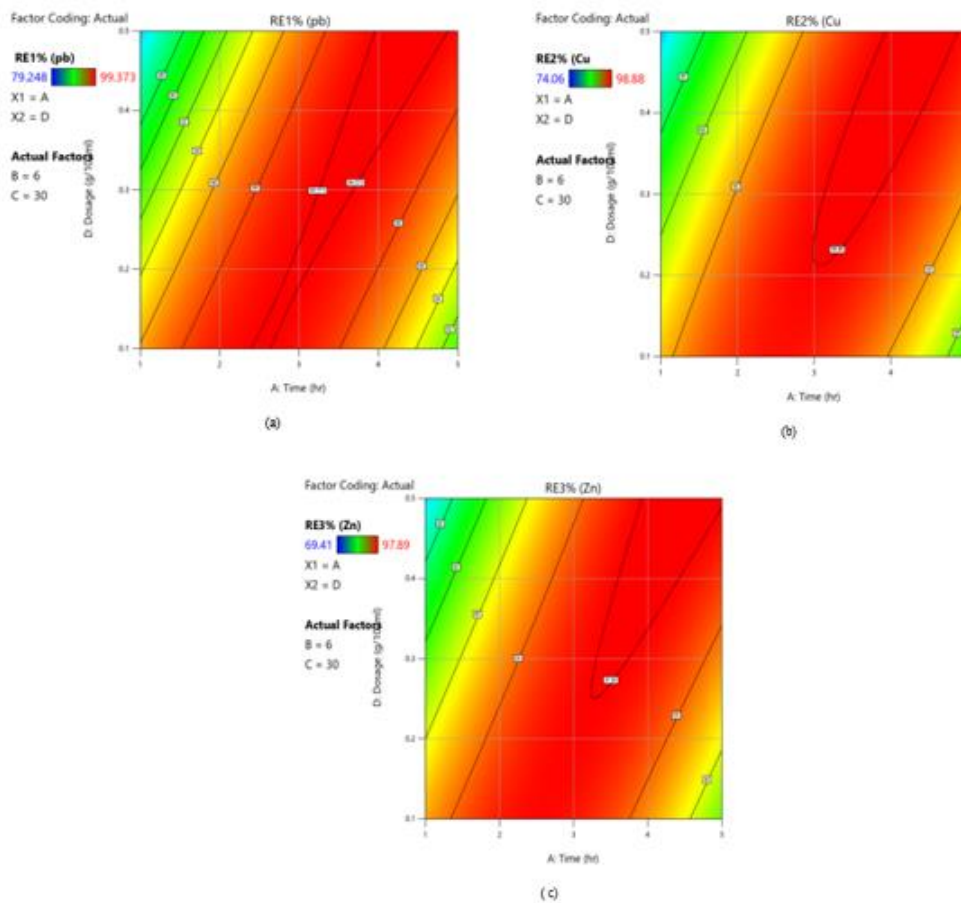


Figure 9 (a, b, c). Contour plots contact time (hr) and adsorbent dosage (pH = 6, metals concentration = 30 mg/L).

Figures 9 a, b, and c, showed the effect of contact time and adsorbent dosage on the removal efficiency at constant pH (6) and metals concentration (30 mg/L). It's observed from these figures the removal efficiency increased with increase in contact time and adsorbent dosage up to 3 hr and 0.3 g/100mL. However, the removal efficiency decreased for contact time, and adsorbent dosage greater than 3 hr and 30 mg/L. This mean that the greater dose may be produce an aggregation in adsorbent particles leading to decrease adsorbent surface area and consequently decrease the removal efficiency [Mohammadi *et al.* 2010].

Figures 10a, b, and c, show the effect of metal concentration and pH on the removal efficiency at

constant contact time (3 hr) and adsorbent dose (0.3 g/100mL). It's noted from these figures the removal efficiency significantly increased with increase in concentration as compared with increasing of pH at its reached to the maximum removal efficiency at 30 mg/L and pH equal to 6. Then the removal efficiency decreased for further increasing of concentration and pH. This implied that a sufficient adsorbent surface area was available at low metals concentrations, which led to an increase in the removal efficiency and at high concentrations the majority of metal ions were not absorbed due adsorbent site saturation as well as the effect of pH increasing [Moreno-Piraján *et al.* 2011; Ugwu *et al.* 2020; Bnar 2021].

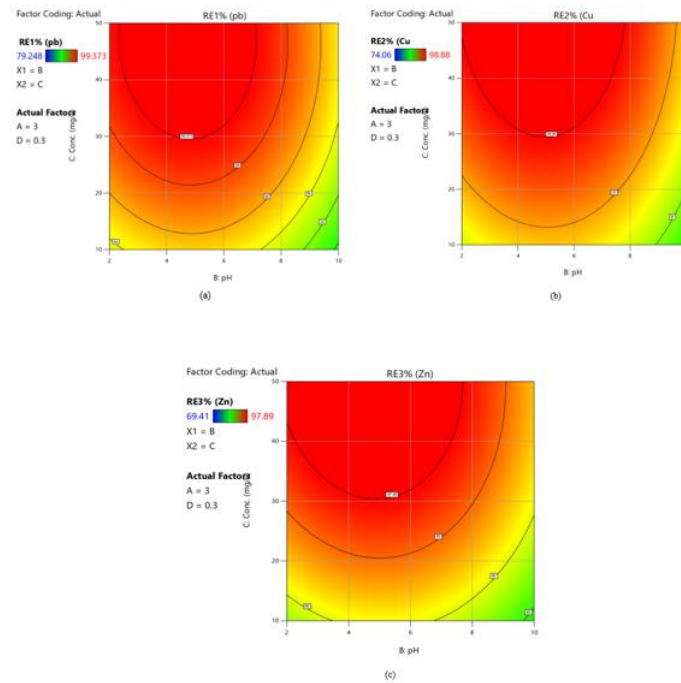


Figure 10 (a, b, c). Contour plots c metal concentration and pH (contact time =3 hr and adsorbent dose = 0.3 g/100mL)

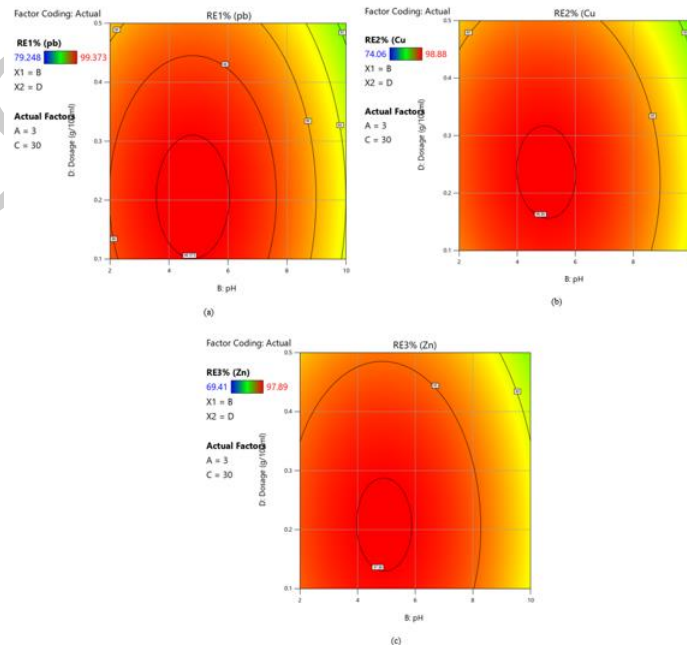


Figure 11 (a, b, c): Contour plots of adsorbent dose and pH (contact time =3 hr and metals concentration = 30 mg/L)

Figures 11 a, b, and c, show the effect of adsorbent dose and pH on the removal efficiency at constant contact time (3 hr) and metals concentration (30 mg/L). It's noted from these figures the removal efficiency strongly increased with increasing of adsorbent dose and of pH at its reached to the maximum removal efficiency at 0.3 g/100mL and pH equal to 6. Then the removal efficiency slightly decreased for further increasing of adsorbent dose and

pH. This means that the amount of adsorbent dose may be produce an aggregation between its particles leading to decrease adsorbent surface area and consequently decrease the removal efficiency. Whereas, the heavy metal ions may be precipitate as hydroxides for pH greater than 6 [Moreno-Piraján *et al.* 2011; Imamoglu and Tekir 2008].

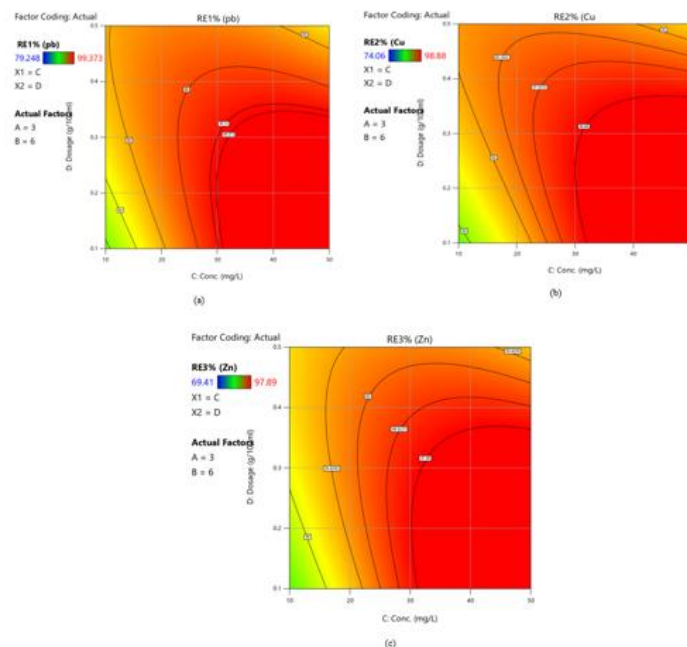


Figure 12 (a, b, c). Contour plots of metals concentration and adsorbent dose (contact time =3 hr and pH = 6)

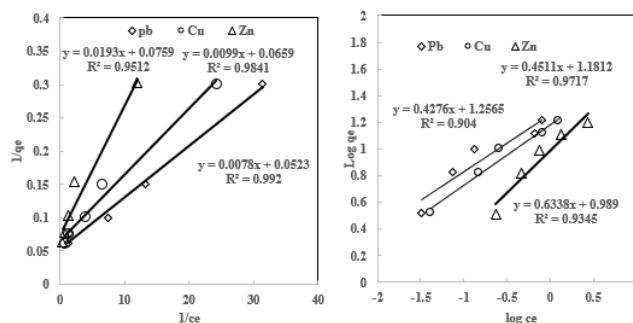


Figure 13. Plots of (a) Langmuir and (b) Freundlich isotherm models

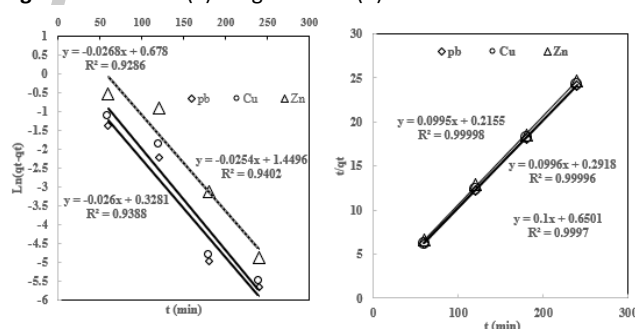


Figure 14. Kinetic model plots of (a) pseudo-first-order and (b) pseudo-second-order

Finally, Figures 12 a, b, and c, show the effect of metals concentration and adsorbent dose on the removal efficiency at constant contact time (3 hr) and pH (6). It's noted from these figures the removal efficiency strongly increased with increasing of adsorbent dose and metals concentration to reach the maximum removal efficiency around adsorbent dose 0.3 g/100mL and metals

concentration equal to 30 mg/L. Thereafter, the removal efficiency slightly decreased for further increasing of metals concentration and adsorbent dose. It's inferred that at low metal concentrations, there was enough adsorbent surface area available, increasing removal efficiency, whereas at high concentrations, the bulk of metal ions were not absorbed due to adsorbent site

saturation. Whereas, the increasing in adsorbent dose may be produce an aggregation between its particles leading to decrease adsorbent surface area and consequently decrease the removal efficiency [Abdel-Ghani and Elchaghaby 2007; Mouni *et al.* 2012; Jiménez-Reyes and Solache 2018].

3.3. Isotherm Models

Various adsorption isotherm models explained the adsorbate's dispersion into solid and phases. In order to fit experimental data for metals ions adsorption under equilibrium circumstances, Langmuir and Freundlich isotherm models were chosen for this purpose. Langmuir model as represented in equation 5 is applied to elucidate monolayer adsorption into the pores of the homogenous surface of the adsorbent at isothermal and equilibrium conditions assuming that the adsorption process occurred without any interaction between adsorbent molecules and sorption at one site is unaffected by adsorption at nearby sites. [Langmuir 1978]. Freundlich model as elucidate in equation 6 is applied to expound multilayer adsorption into the pores of the heterogeneous adsorbent surface at isothermal and equilibrium conditions assuming that the capacity of adsorption is depend on the power of adsorbate concentration [Saleh 2015].

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k_L q_m c_e} \quad (5)$$

$$\ln q_e = \ln k_f + \left(\frac{1}{n} \right) \ln C_e \quad (6)$$

where q_m (mg/g) and q_e (mg/g) are the maximum capacity of the adsorption and the capacity at equilibrium conditions. C_e (mg/l) is the concentration at equilibrium condition, k_L (l/mg), (l/mg), and $1/n$ are the equation constants.

The data of metals concentrations (Pb^{2+} , Cu^{2+} and Zn^{2+}) with adsorption capacities are plotted as shown in **Figure 13a, b**, and the isotherm models coefficients sorted from these Figures are illustrated in Table 11. It's found that the data was well fitted with the Langmuir model as compared with the Freundlich model for Pb^{2+} , Cu^{2+} and Zn^{2+} with $R^2 = 0.992$, 0.9841 , and 0.9512 , respectively. This behavior elaborated that metals adsorption were occurred in monolayer at the adsorbent surface without any interaction between metal ions, and the heat of absorption are uniform for all adsorbent sites [Permeable Reactive Barrier 2020; Jawad and Naife 2022]

Table 11. Correlation constants and correlation of isotherm models

Langmuir Freundlich						
Adsorbate	k_L (l/mg)	q_m (mg/g)	R^2	k_f (mg/g)	n	R^2
Pb	6.7156	19.1237	0.992	3.5131	2.3206	0.9041
Cu	6.6520	15.1766	0.9841	3.2583	2.2170	0.9717
Zn	3.9258	13.174	0.9512	2.6884	1.5778	0.9345

Table 12. Kinetic model constants and correlation coefficients

First Order Second Order						
Adsorbate	k_1 (min ⁻¹)	q_e	R^2	k_2 (min ⁻¹)	q_e	R^2
Pb	0.0259	1.38828	0.9388	0.04595	10.0482	0.99998
Cu	0.0268	1.96998	0.9286	0.0340	10.036	0.99996
Zn	0.0254	4.26144	0.9402	0.0153	10.0009	0.9997

3.4. Adsorption Kinetic Models

Two kinetic models were chosen to explain the adsorption mechanism of Pb^{2+} , Cu^{2+} and Zn^{2+} on the surface of the adsorbent as shown in equations 7, and 8. Pseudo-first-order kinetic model applied with assumption that the rate of ions or adsorbate molecules adsorbed onto the adsorbent is limited by physisorption. Whereas, Pseudo-second-order kinetic model applied with assumption that the rate of ions or adsorbate molecules adsorbed onto the adsorbent is limited by chemisorption [Liu *et al.* 2019; Revellame *et al.* 2020]

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

$$t / qt = (1 / k_2 q_e^2) + (t / q_e) \quad (8)$$

where q_t (mg/g) and q_e (mg/g) are the capacities of the adsorption with time and at equilibrium condition, t (min) is the adsorption time, k_1 (l/min) and k_2 (mg/g.min) are model's coefficients.

The data of adsorption time for metal ions of Pb^{2+} , Cu^{2+} and Zn^{2+} were plotted with adsorption capacities at equilibrium and different intervals of metals adsorption as shown in **Figure 14a, b** and the kinetic model coefficients sorted from these Figures are illustrated in Table 12. It's found that the data was well fitted with the pseudo-second-order kinetic model compared with the pseudo-first-order for Pb^{2+} , Cu^{2+} and Zn^{2+} with $R^2 = 0.99998$, 0.99996 , and 0.9997 , respectively. This behavior elaborated that metals adsorption were conducted as chemisorption for all adsorbent sites [Crini and Badot 2008; Chiou and Li 2003; Lin *et al.* 2017],

4. Conclusion

I-Optimal design approach was selected to design and analysis the experimental data of Pb^{2+} , Cu^{2+} and Zn^{2+} adsorption on activated carbon prepared from pomegranate peels activated by sulfuric acid microwave technique. The raw material and activated carbon were characterized FESEM with EDX, BET, FTIR and XRD

techniques. The effect of contact time, metals concentration, pH, and adsorbent dosage on the simultaneous removal efficiencies. The results elaborated that the pomegranate activated carbon can be used as efficient adsorbent for pb, Cu, and Zn with order of removal efficiencies of 99.373 % for Pb^{2+} , 98.88 % for Cu^{2+} and 97.89% for Zn^{2+} at optimum conditions of adsorption time = 3 hr, pH = 6, metal ions concentration = 30 mg/L, adsorbent dose = 0.3 g/100ml. Langmuir and Freundlich isotherm models were used to analyzed the equilibrium adsorption data, and results showed that the Langmuir model provided a more accurate description as compared with Freundlich model. In addition, the pseudo-second-order model was found as more accurate model for adsorption kinetics representation.

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